Applied Catalysis B: Environmental 219 (2017) 425–431

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Growth of C_3N_4 nanosheets on carbon-fiber cloth as flexible and macroscale filter-membrane-shaped photocatalyst for degrading the flowing wastewater

Xiaofeng Shen[a,b], Tianya Zhang[a], Pengfei Xu[b], Lisha Zhang[b,*], Jianshe Liu[b], Zhigang Chen[a,*]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, 201620, China
[b] State Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China

ARTICLE INFO

Article history:
Received 24 May 2017
Received in revised form 12 July 2017
Accepted 21 July 2017
Available online 24 July 2017

Keywords:
CF/C_3N_4 cloth
Nanosheets
Filter-membrane-shaped photocatalyst
Visible light
Photocatalysis

ABSTRACT

For degrading the flowing wastewater, the ideal photocatalysts should be nanostructured filter-membrane with large area, excellent flexibility and high visible-light-driven photocatalytic activity. Herein, we report the design and preparation of C_3N_4 nanosheets on carbon-fiber (CF) cloth as filter-membrane-shaped photocatalyst. The growth of C_3N_4 nanosheets has been realized by using a dip-coating and thermal condensation method with carbon-fiber cloth as the substrate. The resulting cloth (area: $4 \times 4\,cm^2$) is composed of carbon fiber (diameter: 15 μm) bunches which are decorated with C_3N_4 nanosheets with the thickness of 30 nm. CF/C_3N_4 cloth exhibits excellent flexibility and strong visible-light absorption at ~450 nm. When CF/C_3N_4 cloth (area: $4 \times 4\,cm^2$) is floated on the polluted water, it can degrade 98% Rhodamine B (RhB) in 60 min and 99.3% colorless parachlorophenol (4-CP) after 120 min of visible-light irradiation. Interestingly, when CF/C_3N_4 cloth (area: $4 \times 4\,cm^2$) as the filter-membrane is used to construct a new photocatalytic setup for degrading the flowing wastewater (rate: $1.5\,L\,h^{-1}$) under visible-light irradiation, the degradation efficiency of RhB goes up from 18% to 92% with the increase of filtering/degrading grade from 1 to 7. Direct contact between CF/C_3N_4 cloth and pollutants is found to be unnecessary for the efficient degradation. Furthermore, free radical capture experiments confirm that both $^{\bullet}O_2^-$ and h^+ play a major role in the system under visible light irradiation; and CF/C_3N_4 cloth exhibit excellent stability. Therefore, CF/C_3N_4 cloth has great potential to be used as an efficient, stable, macroscale filter-membrane-shaped photocatalyst for degrading the flowing wastewater.

1. Introduction

The global water resource situation is getting worse and worse; the total volume of wastewater generated globally was about $1500\,km^3$ in 1995, and it increased to ~$2212\,km^3$ in 2010 [1]. To decontaminate wastewater, many methods have been developed, including coagulation sedimentation technology, adsorption technology, ion exchange technology, membrane separation technology, activated sludge technology, biofilm technology, advanced oxidation technology, biological treatment technology, electrochemical technology and photocatalytic technology [2–4]. Usually, the combination of these methods has been used for the practical decontamination of wastewater. Among these methods, photocatalytic technology has been demonstrated to be an efficient and cheap method to degrade organic contaminations and disinfect bacteria for the deep purification of water. In the photocatalytic process, the photocatalysts absorb a certain amount of energy of the photon, so that the electrons transfer from the valence band to the conduction band and the positively charged holes are left in the valence band, participating in the redox reaction [5]. Obviously, the prerequisite for photocatalysis method is to develop excellent photocatalysts.

Generally, three kinds of semiconductor photocatalysts have been well developed. One kind is powder-shaped semiconductor nanomaterials, including nanoparticles [6,7], nanowires [8–10], nanosheets [11–13], nanorods [14,15], nanotubes [16] and so on. These nanopowders usually show excellent photocatalytic activity due to their nanoparticles and large specific surface area. Unfortu-

* Corresponding authors.
E-mail addresses: lszhang@dhu.edu.cn (L. Zhang), zgchen@dhu.edu.cn (Z. Chen).

http://dx.doi.org/10.1016/j.apcatb.2017.07.059
0926-3373/

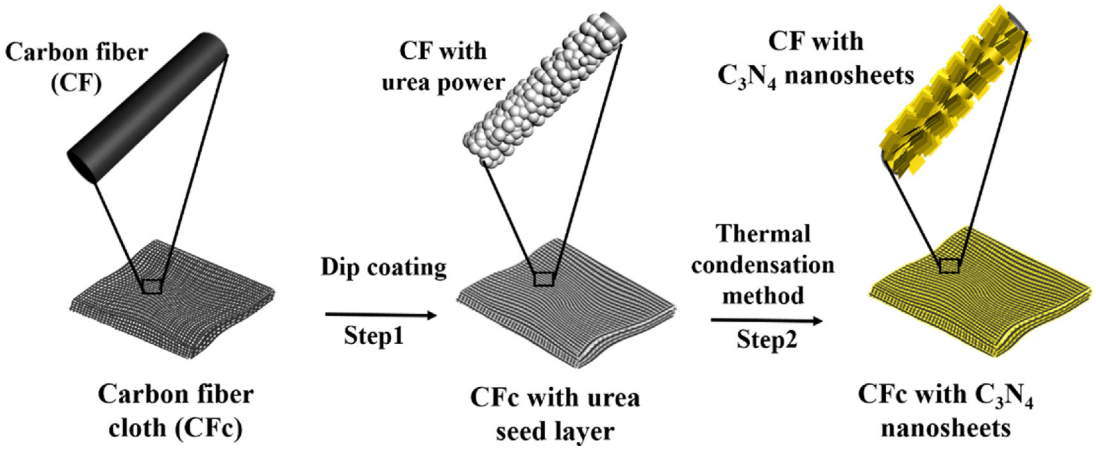

Fig. 1. Schematic illustration of the preparation process of CF/C_3N_4 cloth.

nately, these nanopowders are difficult to recycle and easy to lose in practical application (such as degrading the flowing wastewater), resulting in high-cost and second pollution. The second kind is semiconductor films on the substrates, such as nanoparticles films on ITO glass [17], nanowires/nanotubes-based film on metal foil [18]. These film-shaped photocatalysts have the tuned photocatalytic activity and can be efficiently recycled, but they still have some limitations (such as high production cost) and will prevent the flowing of wastewater. The last kind is free-standing semiconductor film (such as TiO_2 [19]) or nonwoven cloth (such as TiO_2 [20] and WO_3 [21]) with porous structure. We have also prepared Ta_3N_5-Pt [22], Ta_3N_5-Bi_2MoO_6 [23] and Fe_2O_3-AgBr [24] nonwoven cloth as efficient and easily recyclable macroscale photocatalysts. However, the mechanical properties of these free-standing film/nonwoven cloths are unsatisfactory, and especially large-area film/cloth are easily fragile in the flowing wastewater. Therefore, it is very necessary to develop novel photocatalysts with large area, excellent flexibility and high visible-light-driven photocatalytic activity for degrading the flowing wastewater.

As we all know, the filtration technology has been widely used in the purification of flowing water, and it can prevent part of pollutants and allow clean water to pass through easily [25,26]. Many types of filter-membranes have been well developed, such as inorganic (Al_2O_3 [27,28] and SiO_2 [29]) filter-membrane and polymer (polyethyleneimine [30] and polysulfone [31]) filter-membrane. However, these filter-membranes can only block and concentrate the pollutants, and they can not degrade pollutants. If the filtration technology is combined with photocatalysis process, undoubtedly the pollutants can be blocked, concentrated and then degraded, resulting in better decontamination effect and greater potential for the practical purification of the flowing wastewater. The key for the synergetic filtration-photocatalysis technology is to develop the filter membrane that not only has porous structure for blocking and concentrating the pollutants, but also has high photocatalytic activity. The design and preparation of such filter-membranes still remains a serious challenge.

Recently, C_3N_4 as a visible-light-driven photocatalyst has attracted increasing interests due to its low production cost, unique electronic structure and excellent photocatalytic activity and stability [32–34]. In addition, carbon-fiber cloth (CF cloth) is the most popular substrate with excellent flexibility and conductivity, high strength [35–38]. With C_3N_4 and carbon-fiber cloth as the model, herein we firstly designed and prepared C_3N_4 nanosheets on carbon-fiber cloth as filter-membrane-shaped photocatalyst. The resulting CF/C_3N_4 cloth exhibit excellent flexibility, strong visible-light absorption, and high photocatalytic activity for degrading RhB and 4-CP. More importantly, a new photocatalytic setup was constructed for degrading the flowing wastewater (rate: 1.5 L h^{-1}) with CF/C_3N_4 cloth as the filter-membrane. The degradation efficiency of RhB in the flowing wastewater reaches up to 92% after 7 times of filtering/degrading process under visible-light irradiation. In addition, the effect of direct contact, photocatalytic mechanism and stability were further investigated.

2. Experimental sections

2.1. Growth of C_3N_4 nanosheets on CF cloth

Materials and chemicals are shown in Supporting Information. The growth of C_3N_4 nanosheets on CF cloth was realized by a dip-coating and thermal condensation method as follow. To obtained urea-seed layer, a square piece of CF cloth (area: $4 \times 4\ cm^2$) was ultrasonically washed in a mixture solution (deionized water, ethanol and acetone; v/v/v, 1:1:1) for 30 min. Then CF cloth was immersed in saturated urea solution (100 mL) for 30 min and dried at 60 °C for 2 h (step 1 in Fig. 1). The as-coated CF cloth was embedded with urea power and calcined at 550 °C for 3 h in the muffle furnace (step 2 in Fig. 1). The as-prepared cloth was blew and then ultrasonically washed in water for removing the loosened C_3N_4 powder, and dried in the oven at 60 °C for 2 h. For comparison, TiO_2 (P25) was bought in PMMA-Plexiglas company, and pure C_3N_4 was prepared by thermal condensation method [39]. The characterizations of photocatalysts were shown in Supporting Information.

2.2. Measurements of photocatalytic activity

For evaluating the photocatalytic activity, CF/C_3N_4 cloth ($4 \times 4\ cm^2$) was floated on the surface of aqueous solution containing rhodamine B (RhB, 10 mg L^{-1}) or parachlorophenol (4-CP, 1 mg L^{-1}). Measurements of photocatalytic activity, the tests of radical trapping and photocatalytic stability were carried out and shown in Supporting Information.

For degrading the flowing wastewater, a novel photocatalytic reactor was designed and constructed. CF/C_3N_4 cloth was fixed in the middle of the photocatalytic reactor as a filter membrane. RhB solution (10 mg L^{-1}) was used as the model and flowed from bottom to top through filter-membrane-shaped CF/C_3N_4 cloth forcibly with the flow rate of 1.5 L h^{-1}, so as to achieve the purpose of adsorption and degradation. To investigate the effect of number of photocatalytic reactor, a serial of photocatalytic reactor could be connected together, and RhB solution flowed from wastewater tank to each photocatalytic reactor, and finally into the fresh water pool. 1 mL suspension was collected after every photocatalytic reactor to test.

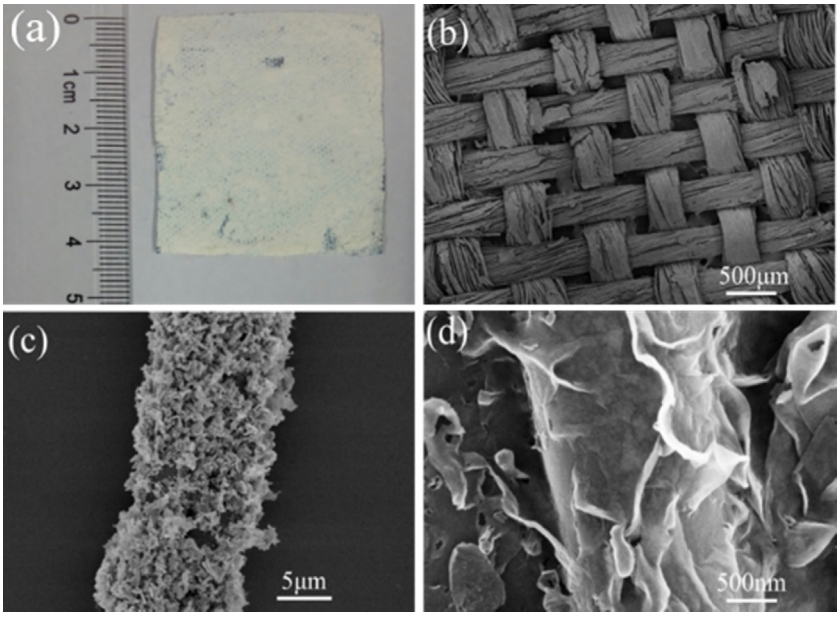

Fig. 2. The photo (a) and SEM images (b–d) of CF/C_3N_4 cloth.

Simultaneously, blank control and dark control experiments were set under the other identical conditions.

3. Results and discussion

3.1. Preparation and characterization of catalysts

With flexible and conductive CF cloth as the substrate, CF/C_3N_4 cloth was prepared by a thermal condensation method (Fig. 1). For facilitating the subsequent heating in the crucible, the commercial CF cloth was tailored to have the area of $4 \times 4\,cm^2$ (Fig. S1a). Obviously, CF cloth is weaved with many CF bunches with the diameter of ~400 μm, and there are many pores among and inside these CF bunches (Fig. S1b). In fact, each bunch is composed of ~1000 CFs with the coarse surface and the diameter of ~15 μm (Fig. S1c).

To in-situ grow C_3N_4 on CF cloth, urea-seed layer was firstly deposited on the surface of CF cloth (step 1 in Fig. 1), and then CF cloth embedded with urea was calcined at 550 °C in air for 3 h (step 2 in Fig. 1). The calcination of urea produced the loosened layer and compact layer of C_3N_4 on the surface of CF cloth. To ensure the stability, the loosened C_3N_4 layer was removed by blowing and then ultrasonically washing cloth. The treated cloth (CF cloth with compact C_3N_4) has the weight of 470 ± 10 mg, where the weight of compact C_3N_4 is determined to be 45 ± 10 mg. The resulting CF/C_3N_4 cloth remains the macro-size with area of $4 \times 4\,cm^2$ (Fig. 2a). Especially, CF/C_3N_4 cloth becomes from black to yellow, and obviously there is a layer of yellow film on the original CF cloth. SEM images confirm that CF bunches have very coarse surface with C_3N_4 coating (Fig. 2b). To further analyze the morphology, single fiber was investigated by SEM image with higher magnification. One can find that there are plenty of C_3N_4 nanosheets on the surface of single CF (Fig. 2c), accompanying a lot of micropores among nanosheets. Furthermore, the surface of CF is almost fully enwrapped by C_3N_4 nanosheets with thickness of ~30 nm (Fig. 2d). These facts confirm the well growth of C_3N_4 nanosheets on CF cloth.

Subsequently, the composition and phase of CF/C_3N_4 cloth were investigated by EDS analysis and XRD patterns, respectively. EDS pattern reveals that there are only N and C elements in the CF/C_3N_4 cloth, since CF only contain C element while C_3N_4 consists of C and N elements (Fig. 3a). Elemental mappings of single fiber confirm that elemental C and N are also homogeneously distributed in fiber (Fig. 3b–d). In addition, the XRD patterns (Fig. 4) suggest that the pure CF cloth has only a broad diffraction peak centering at around 22° which is attributed to the (002) plane of the graphite structure [40]. In contrast, pure C_3N_4 sample has two characteristic diffraction peaks at 13.1° and 27.4°, where 13.1° should be attributed to (100) planes due to the in-plane ordering of tri-s-triazine units with the distance of 0.670 nm, and 27.4° is associated with (002) planes due to the interlayer stacking reflection of conjugated aromatic systems with an interlayer distance of 0.323 nm [39]. Importantly, CF/C_3N_4 cloth exhibits one typical broad diffraction peak (~22°) from carbon fiber, and two peaks (13.1° and 27.4°) from C_3N_4. These results confirm the formation of C_3N_4 on CF cloth.

The optical properties of C_3N_4 and CF/C_3N_4 cloth were studied by using an UV–vis-NIR spectrometer (Fig. 5). Pure C_3N_4 exhibited a strong photo-absorption with an absorption edge around 460 nm, which is consistent with the previous report [41]. Similarly, CF/C_3N_4 cloth also displayed a strong photo-absorption with an absorption edge around ~450 nm, and the slight "blue shift" should result from the texture and pore structure of cloth as well as the inadequate coating with C_3N_4 nanosheets. In addition, an absorption tail in the long-wavelength region can be found for CF/C_3N_4 cloth, which may be associated with the scattering of light among the texture and pore structure in CF cloth and is similar to the photoabsorption of CF/CuO/TiO_2 [42]. These facts confirm that CF cloth substrate has no negative effect on the optical properties of C_3N_4. Therefore, CF/C_3N_4 cloth should remain good photocatalytic activity of C_3N_4.

3.2. Photocatalytic performances under visible-light irradiation

To investigate the photocatalytic activity, CF/C_3N_4 cloth was floated on the surface of aqueous solution of RhB dye ($10\,mg\,L^{-1}$) or colorless 4-CP ($1\,mg\,L^{-1}$) (Fig. 6a). For comparison, the blank test (no photocatalyst) was also performed, and pure CF cloth, TiO_2 (P25) or C_3N_4 was respectively also used as photocatalyst to replace CF/C_3N_4 cloth. After magnetically stirred in the dark for 60 min, the solution realized the adsorption/desorption equilibrium between photocatalysts and pollutants. CF cloth can only adsorb 1% RhB, while CF/C_3N_4 cloth can adsorb 8% RhB (Fig. 6b). The hierarchical pores and large surface area of C_3N_4 benefit the adsorption of RhB. Subsequently, the photocatalytic reaction was

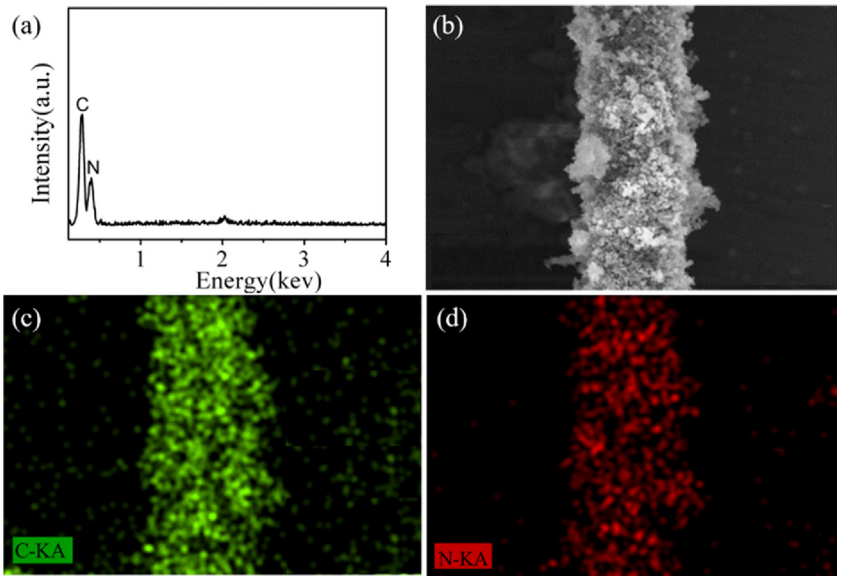

Fig. 3. EDS pattern (a), SEM (b), Elemental mapping (c, d) images of CF/C_3N_4 cloth.

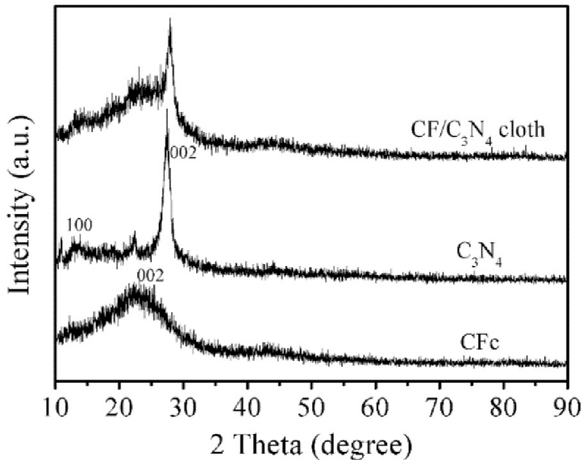

Fig. 4. XRD patterns of CF/C_3N_4 cloth, CFs cloth and C_3N_4 sample.

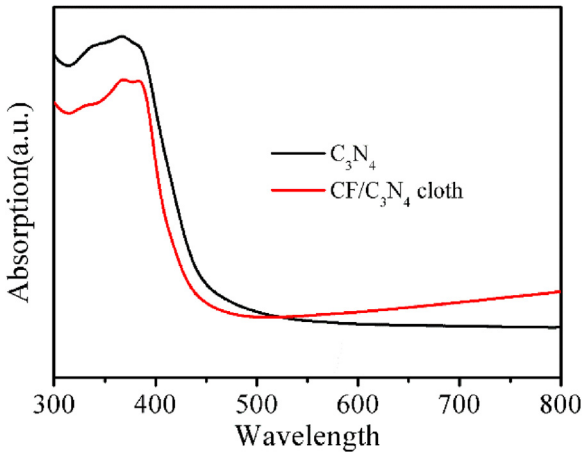

Fig. 5. UV–vis diffuse reflectance spectra of C_3N_4 and CF/C_3N_4 cloth.

carried out under visible-light irradiation (Fig. 6b.) The blank test indicates that no RhB can be removed without photocatalysts under visible-light irradiation. Similarly, pure CF cloth has no obvious photocatalytic activity, and no RhB is degraded. With P25 as the photocatalyst, 25% RhB can be degraded in 60 min (Fig. 6b). Importantly, when CF/C_3N_4 cloth or C_3N_4 powder is used, almost 98% of RhB is degraded after 60 min, suggesting the fact that both samples have the excellent photocatalytic activity and simultaneously the presence of CF cloth substrate has no adverse effect on the photocatalytic properties of C_3N_4. GC/MS analysis reveals that by using CF/C_3N_4 cloth, there are six predominant intermediate products at 30 min of the photodegradation of RhB (Fig. S3 and Table S1). In addition, the reaction kinetics of RhB degradation was studied for different photocatalysts. The degradation datas were analyzed with the pseudo-first-order model [43], $-\ln(C/C_0) = kt$, where C_0 and C are the initial concentrations of contaminants and the concentration of RhB at time t respectively, and k is the reaction rate constant (Fig. 6c). Both k_1 for blank test and k_2 for CF cloth are 0 min^{-1}. The k_3 of P25 is 0.00568 min^{-1}, k_4 of C_3N_4 cloth is 0.10924 min^{-1} and k_5 of CF/C_3N_4 cloth is 0.09718 min^{-1}. Therefore, these facts indicate that CF/C_3N_4 cloth exhibits the highest photocatalytic activity.

Since RhB is a colored pollutant, the fading reaction may be caused by dye sensitization mechanism. To further confirm the essence of photocatalytic reaction by CF/C_3N_4 cloth, colorless 4-CP (1 mg L^{-1}) was used as the model of pollutant (Fig. 6d). The degradation efficiency of 4-CP was investigated by using P25, C_3N_4 powder, CF cloth or CF/C_3N_4 cloth as the photocatalyst. In dark, the adsorption efficiency of CF cloth, P25, C_3N_4 powder are only 2%, 3.4%, 2% in 60 min respectively. With CF/C_3N_4 cloth as the catalyst, only 3% 4-CP can be absorbed in 60 min, which should be attributed to the nature of the electrically neutral of 4-CP. In the subsequent photocatalytic process, the blank test indicates that no 4-CP is removed under visible-light irradiation. With pure CF cloth as the photocatalyst, the degradation of 4-CP is similar to the blank test, no 4-CP is removed after 120 min of reaction. With P25 as the catalyst, 22% 4-CP can be degraded in 120 min. When C_3N_4 power was used as photocatalyst, 99.2% 4-CP is efficiently degraded after 120 min of visible-light irradiation. Importantly, when CF/C_3N_4 cloth was floated on the solution, the degradation efficiency (99.3%) of 4-CP is similar to the efficiency of C_3N_4 power with the same conditions, indicating high photocatalytic activity. These facts prove that CF/C_3N_4 cloth remains the excellent photocatalytic activity of C_3N_4 nanosheets. In addition, GC/MS analysis reveals that by using CF/C_3N_4 cloth, there are four predominant intermediate products at 60 min of the photodegradation of 4-CP (Fig. S4 and Table S2).

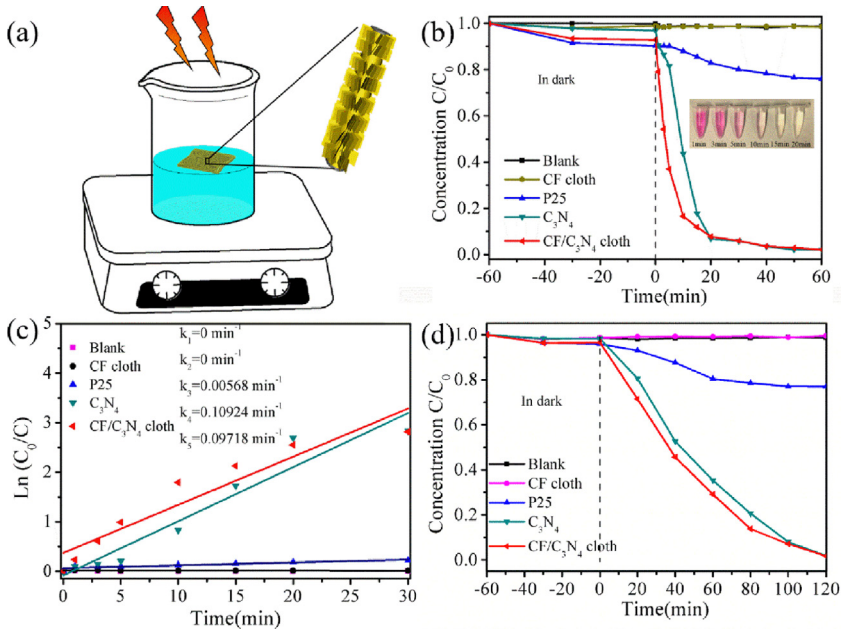

Fig. 6. (a) Schematic illustration of experimental setups, (b) The degradation efficiency of RhB under visible-light irradiation in the absence or presence of CF cloth, P25, C_3N_4 or CF/C_3N_4 cloth (4 × 4 cm^2), (c) rate constants of different catalysts, (d) The adsorption and degradation efficiency of 4-CP under visible light irradiation in the absence or presence of CF cloth, P25, C_3N_4 or CF/C_3N_4 cloth (4 × 4 cm^2).

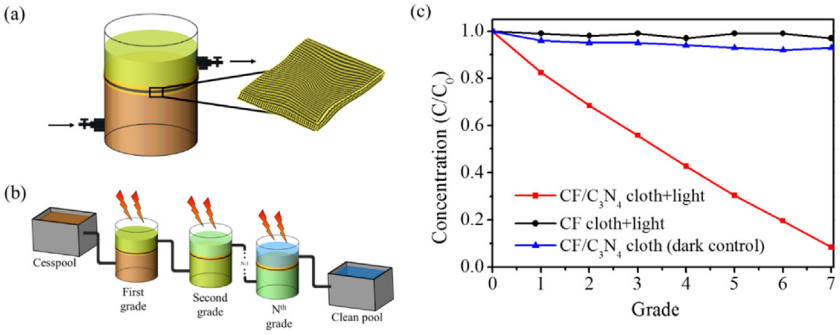

Fig. 7. (a) Schematic diagram of a single photocatalytic reactor, (b) Schematic diagram of the seven photocatalytic reactors for RhB removal in series, (c) The plot of degradation efficiency of RhB by CF/C_3N_4 cloth versus the number of photocatalytic reactor.

As we all know, industry and agriculture produce a lot of flowing wastewater daily, therefore the degradation of flowing wastewater has attracted widespread attention in environmental field. Herein, to degrade the flowing wastewater, CF/C_3N_4 cloth was used as filter-membrane to construct a novel photocatalytic reactor (Fig. 7a), which was set in middle of photocatalytic reactor. In photocatalytic reactor, the flowing wastewater flows from bottom to top through filter-membrane-shaped CF/C_3N_4 cloth forcibly. To improve the degradation efficiency, a series of photocatalytic reactors were connected for constructing multi-grade photocatalytic reactor (Fig. 7b). For comparison, both dark control and pure CF cloth were performed under the same conditions. In dark control test, there is no obvious degradation when the flowing wastewater passes through CF/C_3N_4 cloth. With the pure CF cloth as photocatalyst, the degradation efficiency can be ignored. Importantly, when CF/C_3N_4 cloth is used as filter-membrane-shaped photocatalyst, the degradation efficiency of RhB goes up from 18% to 92% with the increase of filtering/degrading grade from 1 to 7 (Fig. 7c), which indicates that the photocatalytic efficiency can be controlled by the number of membranes and the grade of reactors. On the one hand, this fact demonstrates that filter-membrane-shaped CF/C_3N_4 cloth has an excellent photocatalytic performance with the potential value in industrial wastewater treatment. On the other hand, it proved that the use of multiple reactors can promote photocatalytic degradation efficiency. Thus, the effective combination of filter-membrane-shaped CF/C_3N_4 cloth photocatalyst and new reactor achieves the purpose of adsorption and degradation, improving the photocatalytic degradation of flowing wastewater, which can be applied to degrade pollutants more effectively in river.

It should be pointed out that when the flowing wastewater passes through filter-membrane-shaped CF/C_3N_4 cloth forcibly, the contact time between cloth and pollutants is short. To evaluate whether the direct contact is a necessary condition for the photocatalytic degradation, a photoreactor (Fig. 8a) with separation membrane were constructed according to our previous reports [44,45]. In this photoreactor, 20 mL RhB solution with initial concentration of 10 mg L^{-1} was added in the dialysis bag, and then the dialysis bag was put in the pure water (300 mL) with or without CF/C_3N_4 cloth at the bottom. The dialysis bag allowed small molecules (such as diffusing $^{\bullet}O_2^-$) to come in and out freely, but prevented any nanoparticles and/or CF/C_3N_4 cloth from entering. When the outer system was under various conditions (dark control: with CF/C_3N_4 cloth, without visible light; light control: without CF/C_3N_4 cloth, with visible light; CF/C_3N_4 cloth + visible light), RhB concentration inside dialysis bag and outside dialysis bag were measured (Fig. 8b). In the dark control experiments for 3 h, 76% of

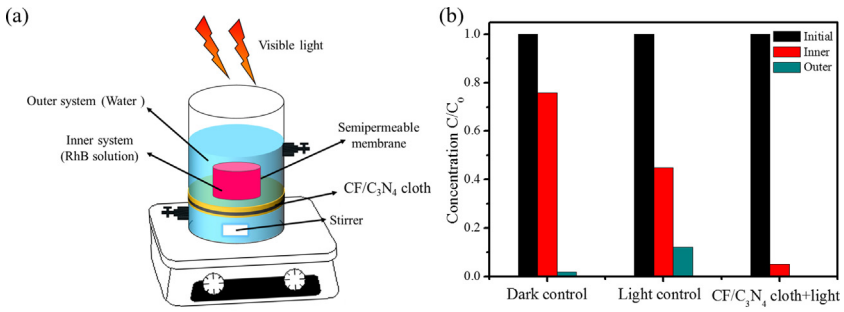

Fig. 8. (a) Schematic illustration of the setup with the separation system, (b) Percentages of RhB inside and outside a semipermeable membrane packaged container when the outer system is in various conditions.

RhB is kept in the dialysis bag and 24% of RhB diffuses into the outer water, due to the leakage of RhB from the dialysis bag. In the light control experiments for 3 h, the percentage of RhB in the dialysis bag decreases to 45%, suggesting the fact that 55% RhB has been diffused to the outer solution where RhB concentration is determined to be 0.37 mg L^{-1}. The rapider leakage of RhB from the inside to the outside should be attributed to the increase of solution temperature due to the long-term light irradiation. When the outer system contains CF/C_3N_4 cloth and is irradiated by visible light for 3 h, no RhB can be detected in the outer solution, revealing that the leaked RhB has been efficiently degraded by CF/C_3N_4 cloth. Importantly, the percentage of RhB in the dialysis bag declines to only 5% which is greatly low compared with the remained amount in dark (76%) and light (45%) control experiments. The obvious reduction from 45% to 5% should not be associated with the rapid leakage, but should be attributed to the presence of CF/C_3N_4 cloth. Under visible light irradiation, CF/C_3N_4 cloth can produce some active species which can diffuse from the outside to the inside of the dialysis bag and then degrade RhB. These facts confirm that the direct contact between CF/C_3N_4 cloth and pollutants is not necessary condition for the photocatalysis.

To investigate the photocatalytic mechanism, it is necessary to detect the main active species formed in the CF/C_3N_4 cloth system. As we all know, the benzoquinone (BQ), ammonium oxalate (AO), silver nitrate ($AgNO_3$) and isopropyl alcohol (IPA) are generally applied to capture superoxide radical anions ($^{\bullet}O_2^-$), photogenerated holes (h^+), electrons (e^-) and hydroxyl free radicals (·OH), respectively [46]. These trapping agents were added to RhB solution in the presence of CF/C_3N_4 cloth by using the photocatalytic system as shown in Fig. 6a. Notably, with $AgNO_3$ or IPA as trapping agents, the degradation efficiency of RhB did not decrease significantly (Fig. 9), proving that e^- and $^{\bullet}OH$ have no effect on the degradation, so both e^- and ·OH could be ignored. However, with the addition of AO and benzoquinone, the decolorization rate of RhB drops sharply and the degradation rate of RhB decreases from 98% to 40% or from 98% to 65% respectively after 60 min (Fig. 9),

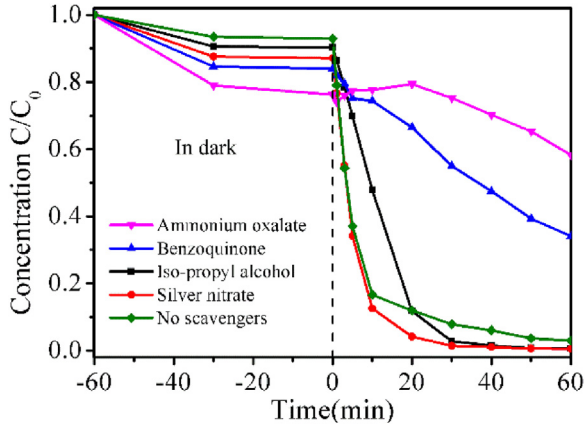

Fig. 9. Comparison of the photocatalytic performance of CF/C_3N_4 cloth for the degradation of RhB (10 mg L^{-1}, 50 mL) with or without various trapping agents (the benzoquinone, ammonium oxalate, silver nitrate or isopropyl alcohol) under visible light irradiation.

which implies that both $^{\bullet}O_2^-$ and h^+ have played an important role in the photocatalytic reaction. Therefore it is concluded that both h^+ and $^{\bullet}O_2^-$ can be considered as the main reactive species. The free radicals have a certain lifetime and can diffuse freely, resulting in the unnecessary direct contact between CF/C_3N_4 cloth and pollutants in the photocatalytic process.

At last, the stability of CF/C_3N_4 cloth is another crucial issue for its practical applications in degrading the flowing wastewater. Herein, the stability of CF/C_3N_4 cloth was also tested through four consecutive cycles of degrading RhB under visible-light irradiation (Fig. 10a). It should be noted that CF/C_3N_4 cloth is easily transferred and/or recycled. At each cycle test, the photodegradation efficiency of RhB remains ~98%, which suggests that CF/C_3N_4 cloth has no significant loss of photocatalytic activity during these four cycles. After four cycles, the weight of CF/C_3N_4 cloth remains unchanged. In addition, the phase and morphology of the used CF/C_3N_4 cloth

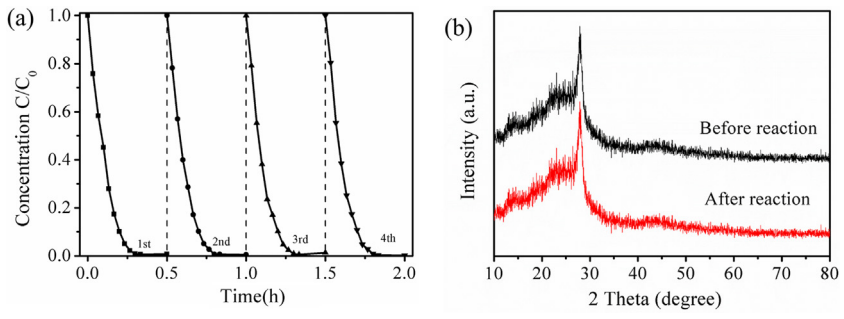

Fig. 10. (a) Cycling runs in photocatalytic degradation of RhB over CF/C_3N_4 cloth. (b) XRD patterns of CF/C_3N_4 cloth before and after photocatalytic reaction.

was further investigated. The used CF/C_3N_4 cloth exhibits the similar XRD pattern (Fig. 10b) and SEM images (Fig. S2) compared with those before photocatalytic reaction. These facts demonstrated that CF/C_3N_4 cloth has excellent stability and recyclability.

4. Conclusions

In summary, filter-membrane-shaped CF/C_3N_4 cloth has been realized by using a dip-coating and thermal condensation two-step method. The photocatalysis characterizations of the resultant CF/C_3N_4 cloth composites were investigated. Under visible light illumination, in static sewage experiments, it exhibits excellent photocatalytic activities on RhB and 4-CP degradation. Importantly, the degradation efficiency of flowing RhB goes up from 18% to 92% with the increase of filtering/degrading grade from 1 to 7 under visible light irradiation with the flow rate of 1.5 L h^{-1}. Furthermore, based on its remarkable and stable photocatalytic performance, this kind of CF/C_3N_4 cloth has great potential to be used as an efficient, stable and macroscale filter-membrane-shaped photocatalysts for degrading flowing wastewater. Moreover, this work provides some insight into the design and development of novel, efficient and easily recyclable macroscale filter-membrane-shaped photocatalysts with nanostructure.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Grant No. 21477019 and 51473033), Program for Innovative Research Team in University of Ministry of Education of China (Grant No. IRT_16R13), Science and Technology Commission of Shanghai Municipality (Grant No. 16JC1400700), Innovation Program of Shanghai Municipal Education Commission (Grant No. 2017-01-07-00-03-E00055), the Fundamental Research Funds for the Central Universities, and DHU Distinguished Young Professor Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2017.07.059.

References

[1] UNESCO-wastewater, http://www.unesco.org/.
[2] H. Wang, L. Zhang, Z. Chen, J. Hu, S. Li, Z. Wang, J. Liu, X. Wang, Chem. Soc. Rev. 43 (2014) 5234–5244.
[3] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Appl. Catal. B: Environ. 202 (2017) 217–261.
[4] C.E. Barrera-Diaz, V. Lugo-Lugo, B. Bilyeu, J. Hazard. Mater. 223–224 (2012) 1–12.
[5] C. Gao, J. Wang, H. Xu, Y. Xiong, Chem. Soc. Rev. 46 (2017) 2799–2823, http://dx.doi.org/10.1039/c6cs00727a.
[6] L.P. Wang, Y. Leconte, Z. Feng, C. Wei, Y. Zhao, Q. Ma, W. Xu, S. Bourrioux, P. Azais, M. Srinivasan, Z.J. Xu, Adv. Mater. 29 (2017) 1603286.
[7] J. Wang, Y. Li, L. Deng, N. Wei, Y. Weng, S. Dong, D. Qi, J. Qiu, X. Chen, T. Wu, Adv. Mater. 29 (2017) 1603730.
[8] H.B. Wu, H.H. Hng, X.W. Lou, Adv. Mater. 24 (2012) 2567–2571.
[9] M. Yu, Z. Wang, C. Hou, Z. Wang, C. Liang, C. Zhao, Y. Tong, X. Lu, S. Yang, Adv. Mater. 29 (2017) 1602868.
[10] H. Xu, S. Liu, Z. Ding, S.J.R. Tan, K.M. Yam, Y. Bao, C.T. Nai, M.-F. Ng, J. Lu, C. Zhang, K.P. Loh, Nat. Commun. 7 (2016) 1–8.
[11] S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang, P.M. Ajayan, Adv. Mater. 25 (2013) 2452–2456.
[12] Q.Y. Lin, L. Li, S.J. Liang, M.H. Liu, J.H. Bi, L. Wu, Appl. Catal. B: Environ. 163 (2015) 135–142.
[13] C. Feng, Z. Wang, Y. Ma, Y. Zhang, L. Wang, Y. Bi, Appl. Catal. B: Environ. 205 (2017) 19–23.
[14] Y. Cui, Z. Ding, X. Fu, X. Wang, Angew. Chem. Int. Ed. 51 (2012) 11814–11818.
[15] P. Li, Y. Li, Z.-K. Zhou, S. Tang, X.-F. Yu, S. Xiao, Z. Wu, Q. Xiao, Y. Zhao, H. Wang, P.K. Chu, Adv. Mater. 28 (2016) 2511–2517.
[16] P. Roy, S. Berger, P. Schmuki, Angew. Chem. Int. Ed. 50 (2011) 2904–2939.
[17] L.-W. Zhang, Y.-J. Wang, H.-Y. Cheng, W.-Q. Yao, Y.-F. Zhu, Adv. Mater. 21 (2009) 1286–1290.
[18] Z. Zhang, L. Zhang, M.N. Hedhili, H. Zhang, P. Wang, Nano Lett. 13 (2013) 14–20.
[19] L. Pellegrino, N. Manca, T. Kanki, H. Tanaka, M. Biasotti, E. Bellingeri, A.S. Siri, D. Marre, Adv. Mater. 24 (2012) 2929–2934.
[20] R. Zhang, X. Wang, J. Song, Y. Si, X. Zhuang, J. Yu, B. Ding, J. Mater. Chem. A 3 (2015) 22136–22144.
[21] S.-J. Kim, S.-J. Choi, J.-S. Jang, N.-H. Kim, M. Hakim, H.L. Tuller, I.-D. Kim, ACS Nano 10 (2016) 5891–5899.
[22] S. Li, L. Zhang, H. Wang, Z. Chen, J. Hu, K. Xu, J. Liu, Sci. Rep. 4 (2014) 1–8.
[23] S. Li, X. Shen, J. Liu, L. Zhang, Environ. Sci.: Nano 4 (2017) 1155–1167.
[24] H. Zhao, L. Zhang, X. Gu, S. Li, B. Li, H. Wang, J. Yang, J. Liu, RSC Adv. 5 (2015) 10951–10959.
[25] L. Ioannou-Ttofa, I. Michael-Kordatou, S.C. Fattas, A. Eusebio, B. Ribeiro, M. Rusan, A.R.B. Amer, S. Zuraiqi, M. Waismand, C. Linder, Z. Wiesman, J. Gilron, D. Fatta-Kassinos, Water Res. 114 (2017) 1–13.
[26] J. Zheng, J. Ma, Z. Wang, S. Xu, T.D. Waite, Z. Wu, Environ. Sci. Technol. 51 (2017) 2757–2765.
[27] Q. Chang, J.e. Zhou, Y. Wang, J. Wang, Desalination 262 (2010) 110–114.
[28] S.S. Madaeni, H.A. Monfared, V. Vatanpour, A.A. Shamsabadi, E. Salehi, P. Daraei, S. Laki, S.M. Khatami, Desalination 293 (2012) 87–93.
[29] A. Farsi, C. Malvache, O. De Bartolis, G. Magnacca, P.K. Kristensen, M.L. Christensen, V. Boffa, Micropor. Mesopor. Mat. 237 (2017) 117–126.
[30] H. Zhang, H. Mao, J. Wang, R. Ding, Z. Du, J. Liu, S. Cao, J. Membrane. Sci. 470 (2014) 70–79.
[31] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, O. Hiroaki, J. Membrane. Sci. 299 (2007) 97–113.
[32] S. Cao, J. Low, J. Yu, M. Jaroniec, Adv. Mater. 27 (2015) 2150–2176.
[33] W.J. Ong, L.L. Tan, Y.H. Ng, S.T. Yong, S.P. Chai, Chem. Rev. 116 (2016) 7159–7329.
[34] Y. Zheng, L. Lin, B. Wang, X. Wang, Angew. Chem. Int. Ed. 53 (2015) 12868–12884.
[35] J. Ren, Y. Zhang, W. Bai, X. Chen, Z. Zhang, X. Fang, W. Weng, Y. Wang, H. Peng, Angew. Chem. Int. Ed. 53 (2014) 7864–7869.
[36] C. Choi, J.A. Lee, A.Y. Choi, Y.T. Kim, X. Lepro, M.D. Lima, R.H. Baughman, S.J. Kim, Adv. Mater. 26 (2014) 2059–2065.
[37] W. Guo, F. Zhang, C. Lin, Z.L. Wang, Adv. Mater. 24 (2012) 4761–4764.
[38] X. Gu, N. Yu, L. Zhang, J. Yang, J. Hu, Z. Chen, RSC Adv. 5 (2015) 102868–102876.
[39] W. Xinchen, K. Maeda, A. Thomas, K. Takanabe, X. Gang, J.M. Carlsson, K. Domen, M. Antonietti, Nature Mater. 8 (2009) 76–80.
[40] C.H. Kim, B.H. Kim, K.S. Yang, Carbon 50 (2012) 2472–2481.
[41] X. Wang, S. Blechert, M. Antonietti, ACS Catal. 2 (2012) 1596–1606.
[42] Z. Yu, J. Meng, Y. Li, Y. Li, Int. J. Hydrogen Energy 38 (2013) 16649–16655.
[43] C. Luo, D. Li, W. Wu, C. Yu, W. Li, C. Pan, Appl. Catal. B-Environ. 166 (2015) 217–223.
[44] L.S. Zhang, K.H. Wong, H.Y. Yip, C. Hu, J.C. Yu, C.Y. Chan, P.K. Wong, Environ. Sci. Technol. 44 (2010) 1392–1398.
[45] L.S. Zhang, K.H. Wong, D.Q. Zhang, C. Hu, J.C. Yu, C.Y. Chan, P.K. Wong, Environ. Sci. Technol. 43 (2009) 7883–7888.
[46] J. Zhang, L. Zhang, X. Shen, P. Xu, J. Liu, CrystEngComm 18 (2016) 3856–3865.